Digest Journal of Nanomaterials and Biostructures Vol. 6, No 3, July-September 2011, p. 1427-1434

STATIC DIELECTRIC ELECTROLYTE PERMITTIVITY IN ELECTRIC DOUBLE LAYER

A. I. IOANID*, R. MIRCEA[a], T. M. CIUCEANU[a]
Faculty of Physics, University of Bucharest
[a]*Electrical Engineering Faculty, „POLITEHNICA" University of Bucharest*

Electrokinetic phenomena implying on fluid flow and their applications in technology, biology and medicine are strongly dependent of the electrostatic properties of the electric double layer (EDL) defined as the volume solvent region situated near to the solid surface, extended over a new charge distribution. Then the solvent is polar, the specific interactions at solid/solvent interface give to high electric fields near to surface and a field-dependence of the static solvent permittivity in the Stern layer from EDL,occurs.

(Received August 18, 2011; accepted September 28, 2011)

Keywords: Electric double layer, Polar solvent, Zeta potential, Field-dependence of permittivity, Fluid-filled gap devices

1.Introduction

Solid-substrate/fluid interface is a physical system that gouverns the electrokinetic phenomena implying on fluid flow and their applications in technology, biology and medicine [1]. Porous materials as porous silicon (PS), are candidates to these applications due their biocompatibility and large surface/volume ratio. At nanometric scale a single macromolecule may be controlled via their electrostatic interactions with EDL defined by the shielding layer that is naturally created within the liquid near a charged surface [2]. The performances of fluidic devices depend both of solid-substrate surface (structure, composition, morphology) and fluid properties (polar, multipolar, electrolyte, polielectrolyte, ion concentration, pH). Generally, the complex interactions at solid-substrate/fluid interface characterise the wetting/dewetting properties of solids; particulary, for aqueous solvent case, the hydrophobic/hydrophilic properties of solid. Other system used as fluidic devices are the colloidal suspensions. It is very important and actual the knowledge of the electrokinetical parameters of the complex colloidal system as blood and pharmaceutical products, but and as cement, dyes, inks, clays, paper,water.

EDL is the volume solvent region situated near the solid surface, extended over the new charge distribution.The spontaneous separation of charge at solid-liquid interfaces is ubiquitous in all micro and nanofluidic devices, and is essential to electrokinetic actuation flow. The solid surface charge generates an electric field which pulls oppositely charged ions (counterions) toward surface and pushes like charges (co-ions) away from it. Counterions preferentially concentrate near surface, effectively shielding the bulk solution from the surface charge. Because the interface charge contains both the positive and negative ions, the main interactions are Coulombic type that are long-range in nature and must be properly calculated to correctly model electrolyte mixtures [3].

Origine of the solid surface charge are the natural reactive surface groups or a strong affinity for ions of one charge or other, the functionalizing reactive surface groups, e.g., amines, carboxylic acids, oxides (hydrophilic surface) , but and other specific phenomena for solid surface that not have reactive surface groups and affinity for ions (hydrophobic surface).

---

*Corresponding author: ana_ioanid@yahoo.com

Then the solvent is polar, at solid/solvent interface are competitive the dipole-dipole interactions. It is shown that strong dipole realignment, ion-ion correlation and finite-size effects can greatly modify the electric field and local permittivity near solid surface [4], so that the EDL is an dielectric heterogeneous medium. The main electrokinetic phenomena controlled of the EDL charge distribution properties are [1]:

- electrophoresis- movement of particle in a stationary fluid by an applied electric field;
- electroosmosis- movement of liquid past a surface by an applied electric field;
- streaming potential- creation of an electric field as a liquid moves past a stationary charged surface;
- sedimentation potential- creation of an electric field when a charged particle moves relative to stationary fluid.

Understanding phenomena near the interface solid/electrolyte is of importance in surface states of solid, electrokinetics, microfluidics, colloidal dispersion and electrochemistry of electrolyte. Dielectric effects due to the local modification of the electrolyte low-frequency permittivity give to the red-green switching of porous silicon luminescence [6].

In this paper we analyse the relation between the hidrophobic/hydrophilic properties of the surface solid and the static dielectric electrolyte permittivity modification and we propose a model for the effective measured permittivity of an aqueous solvent in the EDL.

2.Theory

2.1.EDL Structure and Properties

Structure of the EDL is widely described by the usually Gouy-Chapman-Stern (GCS) model that consists of two layers succeding on the outer normal surface: Stern layer (of bonded by specific-adsorbing ions and Coulomb interactions charges) and diffuse layer in that the ions can move freely in any directions [7].

At immersion of some solid materials in an aqueous electrolyte, on solid surface develope the charge by the dissociation any surface sites and by the adsorbtion of ions from solution.

Ions become specifically adsorbed when their short-range interactions,other than coulombic, are important so that may come into contact with the solid surface. They are usually assumed to form a partial or complete monolayer. This is the hydrophobic surface case.

Ions becomes non-specifically adsorbed, positively or negatively, by their long-range coulombic interactions with surface. They are believed to retain their solvation shell (bonded water molecules) so that have a position near to the surface but separated from it by one or more molecular solvent layer. This is the hydrophilic surface case.

Adding the contributions of the solid lattice deffects (vacances, multivalent impurities) one obtain the intrinsec charge density σ_0 that generate the surface potential ψ_0. IHP is the intern Helmholtz plane, determined by centers of the adsorbing solvent molecules and ions. On IHP plane the charge density is σ_i and the surface potential is ψ_i (Fig.1 (a)). We can consider that solid surface charge density is $\sigma_s = \sigma_0 + \sigma_i$ and surface potential is ψ_s (Fig.1 (b)).

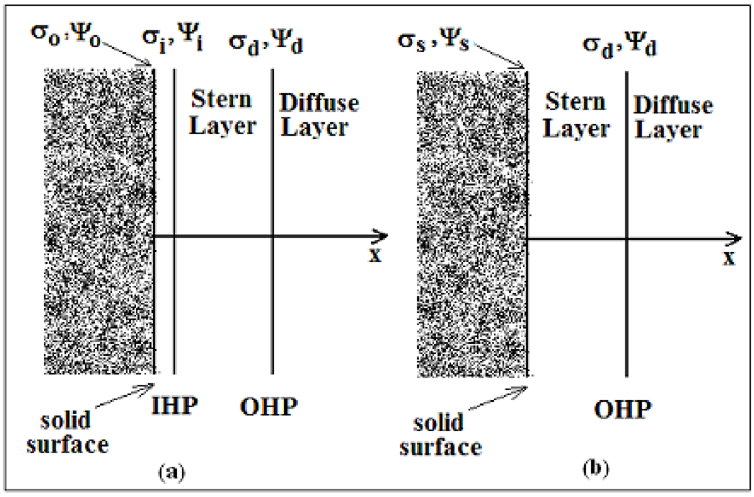

Fig.1.Charge densities and potentials in EDL: (a) detailed and (b) simplified structure.

OHP is the outer Helmholtz plane, determined by centers of the counterions bonded by coulombic interactions, so that the charge density on OHP surface is σ_d , and the potential at OHP is ψ_d . Because between the solid surface (IHP) and OHP plane are no ions, we can consider that for a hydrophobic solid surface , IHP consists in realignmeting solvent dipoles (e.g. water molecules) and OHP in few hydroxyl-ions bonded at the hydrogen-bonded in above IHP dipole molecules [7], while for hydrophilic solid surface IHP consists in dissociated co-ions, adsorbed counterions and OHP consists in electrostaticaly bonded counterions. Layer between IHP and OHP is called Stern Layer and their δ_1 thickness depends on the size of ions. Beyond Stern layer, the solvent charges can move freely mainly by diffusion up the bulk solvent. The zeta potential ς is defined as the surface charge generated potential at the distance at which the electrical forces between ions of opposite charge come into play, (practically at OHP), $\varsigma \approx \psi_{OHP}$, so that this marks the hydrodynamic flow condition at solid/solvent flat interface, and the stability limit for a colloidal suspension respectively. Beyond the OHP plane the electrostatic forces tend to zero and consequently the ς potential tends to zero. For a given solid-surface, the solvent pH at which the ς potential is zero is called isoelectric point (IEP).

To obtain the surface charge potential profil that solution of a Poisson-Boltzmann (PB) equation, it is plausible to take into account the concentration variation with distance from solid surface, zero in Stern layer, decreasing for co-ions and increasing for counterions in diffuse layer, so that the local concentration for an i type ion of valency z_i, at x distance, is

$$n_i(x) = n_i^{bulk} \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right).$$

Poisson-Boltzmann equation for 1-1 electrolyte [1,7], with constant permittivity ε and neglecting polarization effects (effective medium approximation, EMA), may be written:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{e}{\varepsilon_0 \varepsilon} \sum_i n_i^{bulk} z_i \exp\left(-\frac{z_i e \psi(x)}{k_B T}\right).$$

Because for usual solvents, $\frac{z_i e \psi(x)}{k_B T} << 1$, the PB solution is a semnificative potential over the Debye length, defined by:

$$\lambda_D = \left[\frac{e^2 \sum_i n_i^{bulk} z_i}{\varepsilon_0 \varepsilon k_B T}\right]^{-\frac{1}{2}}$$

PB equation approximation breaks down at high electrolyte concentration and must be modified to include the effects of ion size for the ion distribution at very close to the surface [8]. Thus, in the Stern layer, PB equation is:

$$\frac{\partial^2 \psi}{\partial x^2} = 0$$

Considering $\psi(x = \delta_1) = \psi_{OHP} \approx \varsigma$, the potential profil in the Stern layer, $0 \le x \le \delta_1$, is (Fig.2):

$$\psi_{Stern}(x) = \psi_s + (\varsigma - \psi_s)\frac{x}{\delta_1}$$

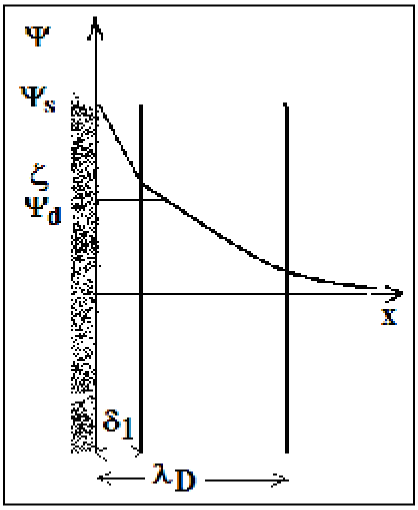

Fig.2. Potential distribution in EDL layer.

Electrical field generated by the surface charge density in Stern layer is:

$$E_{Stern} = -\left.\frac{\partial \psi_{Stern}}{\partial x}\right|_{x=0} = \frac{\sigma_s}{\varepsilon_0 \varepsilon_S}$$

where ε_S is solvent permittivity in Stern layer. The electrical field E_{Stern} modifies the solvent permittivity in Stern layer via an electrostriction effect so that the solvent permittivity ε_S is different from that in the diffuse layer, ε_d.

PB equation in the diffuse layer, $\delta_1 \le x \le \lambda_D$, may be writte (for 1-1 electrolyte):

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{2e}{\varepsilon_0 \varepsilon_d} n_b \sinh\left(\frac{e\psi}{k_B T}\right)$$

Theoretical studies of the electrostatic properties for any systems that are not inherently isotropic, as polarized interfacial systems predict realistic results if the evaluation of the long-range electrostatic interactions take into account the net polarization of the surrounding medium for vacuum boundary conditions [9,10]. In this case, the charge density is given by the dielectric displacement D, so that

$$\frac{\partial D_x}{\partial x} = \rho(x)$$

and the boundary conditions may be writte:

-at solid surface, $x = 0$,

$$\sigma_s = -\varepsilon_0 \varepsilon_S \left.\frac{\partial \psi_{Stern}}{\partial x}\right|_{x=0}$$

-at OHP plane, $x = \delta_1$,

$$\sigma_s + \sigma_d = -\varepsilon_0 \varepsilon_S \left.\frac{\partial \psi_{Stern}}{\partial x}\right|_{x=\delta_1} + \sigma_d = -\varepsilon_0 \varepsilon_d \left.\frac{\partial \psi_{diffuse}}{\partial x}\right|_{x=\delta_1}$$

-at one position from bulk solvent, $\delta_1 < x \to \infty$, taking into account the electrokinetic charge density σ_{ek},

$$\sigma_s + \sigma_d = -\int_{\delta_1}^{\infty} \rho(x')dx' = \sigma_{ek}$$

and neutrality condition is now:

$\sigma_s + \sigma_d - \sigma_{ek} = 0$.

2.2.Field–dependence of the static dielectric permittivity ε_S

A typical value of high surface charge density for a fully ionized surface is $\sigma_s = 0.5Cm^{-2}$ corresponding to one charge per $0.5nm^{-2}$. Computational studies of the permittivity of water stressed by an high electric field [11] use values $\sigma_s \in (0 \div 30\mu C / cm^{-2})$ that generate an high electric field $E_1 \sim 10^9 V / m$.

When a polar liquid is exposed to an external electric field it undergoes polarization mainly by orientational polarization mechanism. At small electric fields the macroscopic polarization P defined as the total dipole moment of the volume unity, is linearly proportional to the applied field and the proportionality constant is a measure of the dielectric permittivity ε, $P = \varepsilon_0(\varepsilon - 1)E$. The decrease in ε with increasing solvent ionic concentration is primarely due to ion-solvation effects. Interactions between ions and solvent molecule inhibe the free rotation of the solvent molecule. For aqueous solvent , the formation of the hydration shell around ions locks orientation of a great number water molecules in the external field. These water molecules are excluded from creating the effective dipole moment of system , thus causing a decrease of polarization and the dielectric constant [12].

For bulk liquid water, at high electric fields the polarization becomes constant and resulting dielectric permittivity falls to unity [13].This behaviour is described by the classical Langevin function $L(x) = coth(x) - \frac{1}{x}, x = \frac{p_{molecule}E}{k_B T}$ where $p_{molecule}$ is the dipole moment of water molecule. At coincidence limit, one obtaine $\varepsilon = 1 + \frac{1}{\varepsilon_0}\frac{\rho p_{molecule}}{E}L(x)$, where ρ is atom number density. This dependence is shown in Fig.3

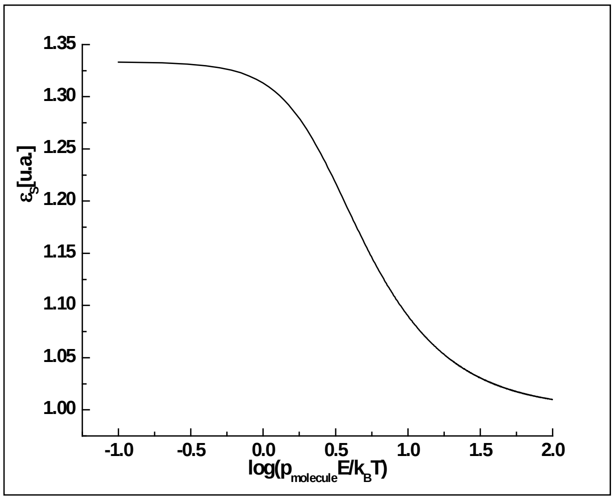

Fig.3. Dependence of the polar solvent dielectric permittivity for high fields.

Parallel orientation due the favorable energetic interaction with the electric field reduces the orientational degrees of freedom of the molecular dipoles for other directions than along axis of the field and is most stable a new ordered configuration in which the orientational polarization is strongly hindered. It is shown that an extremely high interfacial electric field $\sim 10^9 Vm^{-1}$ leads to ordered water layers near to an electrode surface [14]. However, remain active other polarization mechanisms, as the intrabond protonic dynamics that require a lower dielectric permittivity.

Phenomena may be assimilated with at least one water molecule ordered layer by the non-electrostatic (hydrophobic) interactions with a polar (or weakly ionizated) substrate surface. For an ionizated surface, a great number of counterions are fixed by electrostatic (hydrophilic) interactions. In this case, the water molecules are imobilizated in solvation spheres of solvent ions and one can suppose that the dielectric permittivity decreases by the same above high field mechanism.

Dielectric permittivity of a polar solvent decreases in the Stern layer as the surface charge density increases. Decrease is slow for hydrophobic and rapid for hydrophilic substrate surface.

3. Modelling

Electrokinetical phenomena at interface between the electrode and the ionic solution may be measured by any macroscopic observable, as the capacitance of the EDL layer system that is a capacitor those heterogeneous dielectric consists of two different homogeneous dielectrics, Stern layer and diffuse layer, connected in series (Fig.2), so that

$$\frac{1}{C_{EDL}} = \frac{1}{C_{Stern}} + \frac{1}{C_{diffuse}}$$

and effective (measured) dielectric permittivity ε^* is given by equation:

$$\frac{\lambda_D}{\varepsilon^*} = \frac{\delta_1}{\varepsilon_S} + \frac{\lambda_D - \delta_1}{\varepsilon_d}$$

where $\varepsilon_S = \varepsilon$ and $\varepsilon_d \approx \varepsilon_{bulk} \cong 78.$

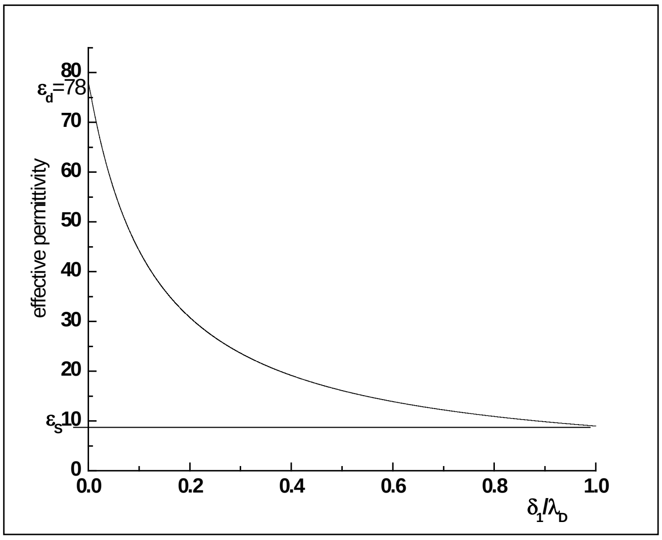

Fig. 4. Dependence of the static effective permittivity on the Stern layer thickness.

Fig.4 shown a qualitative $\varepsilon^*(\sigma_s)$ dependence. We have been considered that λ_D decreases as the solvent ion concentration increases and the δ_1 values are from $\sim 0.2nm$, corresponding to one water molecule layer [15] and $\sim 0.92nm$ for three water molecule layer [13], to $\lambda_D \sim 100nm$ for low ion concentration [1]. Then the capacitor size is comparable with the EDL thickness, the dependence of the capacitance of the ionic strength of solvent is insignificant. This dependence must be taken into account for the capacitor size greater than λ_D. For exemple, for the fluidic devices as biosensors, this $\varepsilon^*(\sigma_s)$ dependence is critical in using the capacitance change as an indicator of the existence of target molecules (biomolecules as ssDNA, oligonucleotides) for an given ionic strength [16].

4.Summary and conclusions

Electrical behaviour of EDL is crucial for different applications, from biosensors and nano-and microfluidic devices, to water-filled gaps for high technology equipment. Electrical properties of EDL depend of both electrode-surface charge density and ion concentration of polar solvent. The inherently physical interactions, hydrophobic or hydrophilic, determine a new ion and dipoles distribution near to surface electrode surface, so that the EDL is a strongly inhomogeneous dielectric medium. Due to electrostatic interactions, the EDL consists into a thin film known as Stern layer, near to electrode-surface, with bound charge and dielectric properties different from the remaining bulk solvent in which the ions are free and a large diffuse layer up to equilibrium ion concentration position. High solvent ion concentration determines a strong electric field in the Stern layer that should produce on orientation of the strongly polar water molecules and a polarization obeying of Langevin law. Dipolar ordering reduces the effective polarization and subsequant dielectric permittivity. The strong field enhancement at the electrode/solvent interface is caused by both surface electrode properties (morphology,free or functionalizated, polar or nonpolar) and solvent characteristics (polar or nonpolar, high or low ion concentration, pH), so that the measured permittivity dependence of this high electric fields is a sensing indicator of the fluid-fillet gap devices.

References

[1] Reto B. Schoch, Jongyoon Han, Philippe Renaud, Reviews of Modern Physics, **80**, 839 (2008).

[2] In Chul Yeh and Gerhard Hummer, PNAS August 17, **101**(33), 12177 (2004).

[3] Paul S. Crozier and Richard L.Rowley, Eckhard Spohr, Douglas Henderson,Comparison of charged sheet and corrected– 3-D Ewald calculations of long-range forces in slab geometry electrolyte systems with solvent molecules ,electronic mail: crozierp@et.byu.edu

[4] R.P. Joshi, J.Qian. and K.H. Schoenbach, Journal of Applied Physics, **96**(7), 3617 (2004)

[5] ***Electrical Double Layer and Zeta potential, Particle Engineering Research Center. National Science Foundation Engineering research center for Particle Research and Technology at the University of Florida

[6] J.N. Chazalviel, F. Ozanam and V.M. Dubin, J. Phys. I France **4**, 1325, (1994)

[7] Vishal Tandon, Skarath K. Bhagavatula, Wyatt C. Nelson, Brian J. Kirby, Electrophoresis, **29**, 1092 (2008).

[8] Jong U. Kim, Electrical Double Layer: revisit based on boundary conditions, e-mail adress: jongkim@ee.tamu.edu

[9] In Chul Yeh and Anders Wallqvist, J.Chem.Phys, **134**, 055109-1 (2005)

[10] Zuowei Wang, Christian Holm, and Hanns Walter Muller, J.Chem.Phys., **119**(1), 379 (2003)

[11] R.P.Joshi, J.Qian, and K.H. Schoenbach, J.Appl.Phys. **96**(7), 3617 (2004).

[12] Peiming Wang, Anderzej Anderko, Fluid Phase Equilibria, **186**, 103 (2001).

[13] Ronen Zangi and Ala E. Mark**,** Journal of Chemical Physics, **120**(15), 7123, (2004)

[14] I.Danielewicz-Ferchmin, A.R. Ferchmin, Chem.Phys.Lett. **351**, 397 (2002)

[15] Claudiu A.Stan, Sindy K.Y.Tang, Kyle J.M.Bishop, George M.Whitesides**,** J. Phys. Chem. B 2011, 115, 1089 (2011)

[16] Mingqiang Yi, Ki-Hun Jeong, Luke P.Lee**,** Biosensors&Bioelectronics, www.elsevier.com/locate/bios, 1-7, (2004).